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DESCRIPTION

PROCESS FOR PRODUCING STRUCTURE, FUNCTIONAL STRUCTURE,
AND MAGNETIC RECORDING MEDIUM

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TECHNICAL FIELD

The present invention relates to a process for
producing a structure having holes, particularly to a
process for producing a functional structure like a
10 magnetic recording medium having holes filled with a
functional material like a magnetic material.

BACKGROUND ART

A new technique, nano-imprinting, is disclosed
15 for forming a nanometer-sized structure on a surface
of an article by impressing directly a structure
having protrusions on a working object, being
different from conventional lithography utilizing a
light beam or an electron beam (U.S. Patent No.
20 5,772,905).

In this technique, as shown in Figs. 9A to 9D,
stamper 100 having a protrusion pattern 103 of a size
of tens or hundreds of nanometers formed by an
electron beam or the like is impressed on thin resin
25 film 104 formed on flat substrate 105 and then
detaching the stamper therefrom to form a projection-
depression pattern: depression portion (molded

region) 106 of the resin film is removed by reactive ion etching or a like method; and substrate 105 is etched by utilizing the unremoved remaining resin layer 107 as the mask to form structure 107, 108
5 having nano-metric projection-depressions corresponding to the original stamper. In this method, to prevent the deterioration of the stamper by impression operation, the impressing action is stopped before top face 141 of protrusion 103 of
10 stamper 100 comes into direct contact with substrate 105 carrying thin resin film 104, and the stamper is detached. In this method, even if the impressing action is stopped before the protrusion top face of the stamper comes into direct contact with the
15 substrate, the resin of the thin film can rise by the impression to come into contact with bottom face 142 of the depression portion of the stamper.

This contact may make irregular the formed protrusion-depression structure of the thin resin
20 film on detaching of the stamper from the thin resin film.

The present invention intends to provide a structure having holes at desired positions.

25 DISCLOSURE OF THE INVENTION

According to an aspect of the present invention, there is provided a process for producing a structure

having holes, comprising steps of (A) providing an
impressing member having protrusions, and a substrate,
(B) forming a layer, on the substrate, from a
material having a less strength than the impressing
5 member, (C) forming depressions by impressing the
impressing member on the layer corresponding to
protrusions of the impressing member, (D) etching the
layer to bare at least a part of the surface of the
substrate, and (E) anodizing the substrate to form
10 holes on the substrate.

According to another aspect of the present
invention, there is provided a process for producing
a functional structure comprising a step of filling a
functional material into the holes formed in the
15 process.

In a structure of the present invention, the
term "protrusion" and "protruded portion" means a
portion protruded from the surround, i.e. depression
defined in the following. The term "depression" and
20 "depressed portion" means a portion comprised of a
bottom having a level lower than that of a top of the
adjacent protrusion. The term "protrusion-depression
structure" means a structure consisting of the
protrusion and the depression. When directing the
25 attention to a pattern of protrusions of the
protrusion-depression structure, the structure may be
called as "protrusions structure", and when doing of

depression, it may be as "depression structure".
Patterns of these structures are called as
"protrusion-depression structure pattern" or
"protrusion-depression pattern" for short;
5 "protrusion structure pattern" or "structure pattern"
for short; and "depression structure pattern" or
"depression pattern" for short, respectively. The
distance between the top of a protrusion and the
bottom of the adjacent depression is the "height of
10 the protrusion" or the "depth of the depression".

The process for producing a structure of the
present invention comprises the steps of forming a
pattern by impressing an impressing member having a
protrusion-depression structure consisting of plural
15 protrusions and depressions on a patterning layer on
a workable layer, and detaching the impressing member
from the patterning layer. In this process, the top
faces of the protrusions of the protrusion structure
(hereinafter referred to as "protrusion top faces")
20 has a size not larger than 500 nm and a height of not
larger than 10 μm , the patterning layer is made
thinner than the height of the protrusions of the
impressing member to prevent the contact of the
surface of the patterning layer with the depressed
25 bottom of the protrusion-depression structure of the
impressing member.

The above-mentioned size of the top face of the

protrusion of the impressing member means a diameter for a circle-shaped face, and an outside diameter for polygon-shaped face. The height of the protrusion is in the range from several nanometers to 10 μm ,
5 preferably from tens of nanometers to 5 μm .

In a preferred process for producing a nano-structure of the present invention, patterning layer is formed on a workable layer in a thickness less than the height of the protrusion of the stamper, and
10 the stamper is impressed on the opposing patterning layer to form in the patterning layer a depression pattern corresponding to the protrusion pattern of the stamper.

The patterning layer thinner than the height of
15 the protrusions of the stamper reduces the adverse effects of air bubbles, rendering unnecessary a vacuum atmosphere. After the impressing operation, the workable layer is bared by etching, and bared portion is worked by anodization or like a treatment.
20 Thus a simple nano-printing method is provided which does not require strict position control in the impressing direction.

BRIEF DESCRIPTION OF THE DRAWINGS

25 Figs. 1A, 1B, and 1C are sectional views for explaining Example 1 of the present invention.

Figs. 2A, 2B, and 2C are sectional views for

explaining Examples 2 and 3 of the present invention.

Figs. 3A and 3B are sectional views for explaining Examples 2 and 3 of the present invention.

Figs. 4A, 4B, and 4C are sectional views for
5 explaining Example 4 of the present invention.

Figs. 5A and 5B are surface views for explaining an example of arrangement of the depressed structure of the present invention.

Figs. 6A, 6B, and 6C are sectional views for
10 explaining Example 5 of the present invention.

Figs. 7A, 7B, and 7C are sectional views for explaining Example 6 of the present invention.

Figs. 8A, 8B, and 8C are sectional views for explaining Example 7 of the present invention.

15 Figs. 9A, 9B, 9C, and 9D are sectional views for explaining an example of prior art.

BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the present invention
20 are described below.

In a preferred embodiment of the present invention as shown in Figs. 4A to 4C, a stamper (impressing member) having a protrusion pattern formed thereon is placed in opposition to a workable
25 layer having a patterning layer provided thereon, and the stamper is impressed on the patterning layer such that at least the tops of the protrusions are brought

as close as about 50 nm or less to the workable layer surface and is detached to form the protrusion pattern on the patterning layer, corresponding to the stamper.

5 In the case where the patterning layer is formed from a material which becomes less viscous in proportion to temperature elevation, preferably the stamper is impressed on the patterning layer heated to obtain suitable viscosity, and after cooling, the
10 stamper is detached.

 The nano-structure prepared as shown in Figs. 2A and 2B is preferably dry-etched or wet-etched to bare the workable layer at the depressed portions of the patterning layer, and the nano-structure obtained
15 above is preferably anodized to form a depression structure in the workable layer as shown in Fig. 2C.

 In the step of baring the workable layer, the dry-etching or wet-etching is conducted preferably to bare the workable layer at the depressed portions of
20 the patterning layer and to form depressions (holes) of depth of 1 nm or more in the workable layer (Fig. 2B).

 The stamper has preferably at least one pair of protrusion-depression structures at intervals of not
25 more than 1 μm between the protrusions.

 The patterning layer is formed preferably from a flowable thin-coating material such as a resin

solution in a solvent, a resin material containing an alkoxide or a silicone, and silsesquioxane.

The workable layer is composed preferably of a metal containing aluminum.

5 The workable layer is constituted preferably of an underlayer composed of a metal other than aluminum and a surface layer containing aluminum.

In a process of producing the nano-structure of the present invention, preferably as shown in Figs. 10 1A to 1C, stamper 1 having a pattern of protrusions 4 is placed in opposition to workable layer 3 having patterning layer 2 of a thickness smaller than the height of protrusions 4 of the protrusion-depression structure; stamper 1 is impressed to bring the tops 15 of protrusions 4 as close as 50 nm or less to the surface of workable layer 3; and the stamper is detached therefrom to form a protrusion pattern corresponding to stamper 1 on patterning layer 2.

Stamper 1 having at least one protrusion or 20 depression is formed by lithography employing an electron beam, an X-ray, ultraviolet light, visible light, or the like, wet-etching or dry-etching, electron beam direct-writing, anodic oxidation, and the like technique. The surface of protrusion 4 is 25 preferably flat: plural protrusions have preferably the top faces placed on one and the same plane. The protrusion structure has preferably an arrangement of

columns in a triangular lattice state as shown in Fig. 5A, or may have a multiple periodic arrangement constituted of several regular constitutions as shown in Fig. 5B. In the Fig. 5B, an arrow denoted by
5 numeral 15 indicates a triangular lattice region, an arrow denoted by numeral 16 indicates a rectangular lattice region, and an arrow denoted by numeral 17 indicates a graphite lattice region. Dots 18 on boundary lines between the regions belong to both the
10 regions.

In the production process of the present invention, preferably as shown in Figs. 1A to 1C, patterning layer 2 is formed by applying a liquid material on workable layer 3 by spin coating or a
15 like method: the liquid material being mainly composed of a flowable thin-coating material such as a resin solution in a solvent, a resin material containing an alkoxide or a silicone, and silsesquioxane. The thickness of patterning layer 2
20 is made smaller than the height of protrusion 4 of stamper 1. Then, stamper 1 is placed in opposition to patterning layer 2; the stamper is impressed to bring the tops of protrusions 4 as close as 50 nm or less to the surface of workable layer 3; and the stamper
25 is detached therefrom to form a depression pattern corresponding to protrusion pattern 4 in stamper 1 on patterning layer 2. The impressing member is

preferably a regularly arranged protrusion structure having a surface layer composed of silicon, nickel, or the like, and is preferably coated with a releasing material such as a fluoro-resin, and a
5 silane coupling agent for improving releasability.

The smaller thickness of patterning layer 2 than the height of protrusions 4 of the stamper reduces the adverse effect of an air bubble imprisoned in depression portion 5 of the stamper to
10 impede the pattern formation. This makes unnecessary a vacuum atmosphere for the impressing and detaching operation. The working object 9 to be worked is preferably heated to a temperature necessary for obtaining a lower viscosity of patterning layer 2
15 before the impression operation.

The structure produced as above is subjected preferably to dry-etching or wet-etching to remove patterning layer 2 remaining at bottoms 7 of depression portions 7 of the patterning layer to bare
20 workable layer 3 (Figs. 2A and 2B).

For example, in the case where workable layer 3 is composed of an electroconductive material such as a metal and patterning layer 2 is composed of an insulating material such as a resin, electroplating
25 can be conducted by utilizing protrusions 6 of patterning layer 2 after pattern formation as a mask and the bared portions of workable layer 3 as an

electrode. Thereafter by immersion into a solution capable of dissolving selectively patterning layer 2, a structure can be obtained which has a protrusion-depression structure corresponding to that of stamper 1 from a different material.

In the case where workable layer 3 is made from a material mainly composed of aluminum, alumina nano-holes can be obtained by anodization starting from the bared portions of the etched workable layer obtained by etching the remaining film at bottom 70 of depression 7 of the patterning layer. If the patterning layer is soluble in the anodization solution, the layer is protected by lamination of thin protection layer 11 made of a metal like aluminum (Fig. 6B) which can be dissolved during the anodization, and then the anodization is conducted (Fig. 6C) as shown in Figs. 6A to 6C.

In the case where the bared portions of the workable layer are also etched more or less during the etching treatment as shown in Figs. 7A to 7C, the patterning layer is removed (Fig. 7B) and then the anodization is conducted (Fig. 7C).

The anodization is conducted specifically by application of a voltage by utilizing the workable layer having the patterning layer as the anode in an acidic solution such as an aqueous oxalic acid solution and an aqueous sulfuric solution. The

oxidation and dissolution by the anodization is initiated predominantly from the depression portions of the patterning layer to form fine holes arranged in the depression pattern. The voltage to be applied is considered generally to be equal to the arrangement cycle multiplied by a factor of 2.5^{-1} [V/nm]. For example, for a triangular lattice arrangement of 100 nm intervals, a voltage of 40 volts is applied. The average cycle length of the formed fine holes depends on the applied voltage. Accordingly, in formation of regular triangular depression pattern on patterning layer 2 and subsequent formation of the fine holes on bottoms of depressions 7, slight disturbance of regular arrangement of the depression structure can be corrected automatically into regular arrangement of the fine holes by action of the applied anodization voltage.

In the case where the patterning layer is made of a material which is dissolvable at a suitable dissolving rate uniformly by the anodization solution, the etching process may be omitted. With start of the anodization, the patterning layer begins to dissolve to bare the workable layer at bottoms of the depressions. Then electric current comes to flow through the bared layer portions to form nano-holes on the workable layer. When the patterning layer is

made of a material which is not soluble in the anodic oxidation solution, no change occurs on the workable layer surface.

The diameter of the formed nano-holes can be
5 enlarged as desired by immersion in a solution capable of dissolving the workable layer, such as an aqueous phosphoric acid solution.

Various functional structure can be produced by filling the holes with a functional material by
10 electrodepositing, sputtering, or a like method. In particular, a magnetic recording medium can be obtained by filling the fine holes with a magnetic material by electrodeposition.

(EXAMPLE)

15 The present invention is described below in detail by reference to drawings.

(Example 1)

An example of the present invention is described below by reference to Figs. 1A to 1C.

20 Stamper 1 having protrusion-depression pattern formed thereon is impressed to opposing workable layer 3 having patterning layer 2 having a thickness less than the height of protrusions 4. After the tops of the protrusions 4 has reached the position 30 nm
25 to the surface of workable layer 3, the stamper is detached, thereby forming a protrusion pattern of stamper 1 on patterning layer 2.

For example, columnar protrusions 4 having a diameter of 30 nm and a height of 75 nm are formed at arrangement intervals of 100 nm on a base plate by electron beam projection and dry-etching to prepare
5 stamper 1. Separately, on Si substrate 8, there are formed workable layer 3 composed of silicon oxide (SiO_2) in a thickness of 100 nm and patterning layer 2 composed of polymethyl methacrylate (PMMA) in a thickness of 50 nm. This PMMA layer is formed by
10 applying a solution thereof in ethyl cellosolve acetate solution by spin coating. Stamper 1 is placed in opposition to patterning layer 2, and impressed thereon at a substrate temperature of 120°C with an impression load of 1000 kgf/cm². After impression for
15 30 seconds and cooling to 60°C, the stamper is detached (Figs. 1A and 1B). The height of the protrusion 6 (non-impressed portion) of patterning layer 2 is increased slightly by the flow of resin corresponding to the volume of formed depressions 7
20 by the impression, and the resin remains in a thin film state on the bottom 70 of depression 7 owing to nonuniformity of the stamper shape.

The thickness of patterning layer 2 is smaller than the height of stamper protrusion 4. Therefore,
25 the air bubble, which is usually imprisoned in depression portion 5 of the stamper and impedes the pattern formation, is allowed to escape through the

depression space of the stamper to the outside.
Therefore, the fine pattern can be formed without vacuum application by the impression operation. The required impression pressure is less because of the
5 smaller contact area. Further, since the height of protrusion 6 (non-impressed portion) of the patterning layer after pattern formation depends on the initial film thickness of patterning layer 2 and the shape of stamper 1, fine adjustment of the
10 impression load and position control of the impression direction are not necessary.

(Example 2)

An example of the present invention is described below by reference to Figs. 2A to 2C and
15 Fig. 3.

The structure having been prepared by the process for production of a nano-structure in Example 1 is subjected to dry-etching or wet-etching to remove the remaining resin material from bottoms
20 of depressions 7 of the patterning layer to bare workable layer 3.

Stamper 1 described in Example 1 is placed in opposition to working object 9 having workable layer 3 composed of aluminum (Al) of 100 nm thick and
25 having patterning layer 2 composed of PMMA. Stamper 1 is impressed thereon at a substrate temperature of 120°C at a load of 1000 kgf/cm² for a holding time of

30 seconds, and after cooling to 60°C, the stamper is detached to obtain a structure shown in Fig. 1C. The structure is subjected to dry-etching in an oxygen atmosphere to remove the resin remaining at bottoms
5 70 of depressions 7 of the patterning layer to bare Al (Fig. 2A). Otherwise, the etching may be conducted in an atmosphere of a mixture of BCl_3 and O_2 to remove simultaneously the Al below bottom 70 of depression 7 of the patterning layer to form hollows (Fig. 2B).

10 Thereafter, tin-copper solder electroplating is conducted by utilizing protrusion portion 6 of the patterning layer as the mask and workable layer 3 as the electrode, and then protrusion 6 of the patterning layer is selectively removed by ultrasonic
15 acetone washing to obtain a solder-protrusion structure having protrusions in an nanometeric intervals.

Otherwise, lamination film 10 is formed from a desired material by sputtering or a like method as
20 shown in Fig. 3A, and protrusion 6 of the patterning layer is selectively removed by ultrasonic acetone washing to obtain protrusion structure shown in Fig. 3B.

(Example 3)

25 An example of the present invention is described below by reference to Figs. 2A to 2C and Figs. 3A and 3B.

Stamper 1 described in Example 1 is placed in opposition to working object 9 having workable layer 3 composed of Al and having patterning layer 2 composed of silsesquioxane. Stamper 1 is impressed thereon with the substrate kept at room temperature with a load of 1200 kgf/cm² for a holding time of 30 seconds. Then the stamper is detached. The worked object is dry-etched in an atmosphere of argon and SF₆ to bare Al (Fig. 2A). The dry-etched object is subjected to anodization by utilizing the Al as the anode in an aqueous 0.3 mol/L oxalic acid solution at a temperature of 16°C by application of a voltage of 40 V. Since the anodization is initiated at the bared portion, nanometer-sized holes are obtained which have a high aspect ratio and are arranged in a pattern of the patterning layer (Fig. 2C). The silsesquioxane, which is insoluble in an aqueous oxalic acid solution, need not be removed.

(Example 4)

An example of the present invention is described below by reference to Figs. 4A to 4C.

Stamper 1 having a protrusion-depression pattern formed thereon is impressed on workable layer 3 having patterning layer 2 thereon, and then detached. Thereby, a depression pattern which is counter to the protrusion pattern of stamper 1 is formed in patterning layer 2.

As an example, from an Si base plate, stamper 1 is prepared by forming columnar protrusions 4 of 30 nm diameter and 75 nm high in a triangular lattice arrangement at intervals of 100 nm by electron beam lithography and dry-etching. The top faces of the highest protrusions 4 are positioned preferably on one and the same plane. Separately, on substrate 8, there are formed workable layer 3 of 100 nm thick composed of silicon oxide (SiO_2) and patterning layer 2 of 100 nm thick composed of polymethyl methacrylate (PMMA) as shown in Figs. 4A to 4C. The PMMA is applied as a solution in ethyl cellosolve acetate by spin coating. Stamper 1 is placed in opposition to patterning layer 2, and is impressed thereon at a substrate temperature of 120°C at a load of 500 kgf/cm². The stamper and the substrate are cooled at that state to 60°C, and then the stamper is detached (Figs. 4A, 4B, and 4C). The resin in a volume corresponding to the volume of depression 7 is allowed to flow, whereby the thickness around the impressed portions of patterning layer 2 increases slightly in comparison with that before the impression. At the bottoms 70 of depressions 7, the resin remains in a thin film owing to nonuniformity of the stamper shape and incomplete flow of the resin.

An air bubble may be imprisoned in depression 5 of stamper 1 depending on the shape of the pattern.

This imprisoned air can impede the flow of the resin, and makes difficult the formation of the pattern in precise accordance with the stamper shape. This adverse effect can be reduced by raising the
5 substrate temperature to increase the flowability of the resin, decreasing the thickness of patterning layer 2 to be less than that of protrusion 4, or other counter measures.

(Example 5)

10 An example of the present invention is described below by reference to Figs. 6A to 6C.

The structure obtained by the process of production of a nano-structure in Example 4 is subjected to dry-etching or wet-etching to remove the
15 resin remaining on bottoms 70 of depressions 7 of the patterning layer to bare workable layer 3.

Stamper 1 described in Example 4 is placed in opposition to working object 9 constituted of Si substrate 8, and workable layer 3 composed of
20 aluminum (Al) of 200 nm thick and patterning layer 2 composed of PMMA formed on the substrate. Stamper 1 is impressed thereon at a substrate temperature of 120°C at a load of 500 kgf/cm², and is detached after cooling to 60°C to obtain a structure shown in Fig.
25 4C. This structure is subjected to dry-etching in an oxygen atmosphere to remove selectively the resin remaining at bottoms 70 of depressions 7 of the

patterning layer to bare Al (Fig. 6A). Then as shown in Fig. 6B, protection layer 11 is formed from Al in a thickness of 5 nm by sputtering. Anodization is conducted by utilizing this layer as the anode in an aqueous oxalic solution (0.3 mol/L, 16°C) by application of 40 V. Thereby alumina nano-holes are formed as shown in Fig. 6C. The nano-holes are formed from bottoms 70 of depressions 7 of the patterning layer in a triangular lattice arrangement at intervals of 100 nm. Protection layer 11 serves to protect patterning layer 2 from corrosion in the acidic solution, and can be removed later by ultrasonic washing in a solution capable of dissolving aluminum such as an aqueous phosphoric acid solution. The PMMA can also be removed by ultrasonic washing in a solvent such as an aqueous phosphoric solution, and acetone.

(Example 6)

An example of the present invention is described below by reference to Figs. 7A to 7C.

In the preparation of the nano-structure described in Example 5 or Example 2, both the resin remaining at bottoms of depressions 7 of the patterning layer and Al can be simultaneously removed by etching in an mixed etching atmosphere containing BCl_3 and O_2 to form hollows on the Al surface (Fig. 7A). Thereafter, the PMMA is removed by ultrasonic

acetone washing or ozone-ashing (Fig. 7B). This working object as the anode is subjected to anodization in an aqueous oxalic acid solution (0.3 mol/L, 16°C) by voltage application of 40 V to form alumina nano-holes as shown in Fig. 7C. The nano-holes are formed starting from hollows 13 on the surface of the Al, and are arranged in triangular lattice at intervals of 100 nm.

(Example 7)

10 An example of the present invention is described below by reference to Figs. 8A to 8C.

 A stamper having a protrusion-depression pattern is placed in opposition to a workable layer having a patterning layer, and is impressed thereon and detached therefrom to form, on the patterning layer, a depression pattern corresponding to the protrusion pattern of the stamper.

 Next, on a substrate composed of Si, a titanium film is formed in a thickness of 10 nm, and further thereon an aluminum film is formed in a thickness of 500 nm as a workable layer. Further thereon, a patterning layer is formed from aluminum alkoxide in a thickness of 75 nm. The aluminum alkoxide is applied as an IPA (isopropyl alcohol) solution by spin coating. The stamper employed in Example 4 is placed in opposition to the patterning layer, and impressed thereon at a substrate temperature of 150°C

with a load of 1000 kgf/cm². The stamper and the object are cooled to 60°C by keeping the impressing state. Thereafter the stamper is detached. The patterning layer becomes slightly thicker around the impressed points after the impression corresponding to the volume of the flow of the resin caused by the impression. The resin remains at the bottom portions of the depression in a thin film owing to nonuniformity of the stamper shape and incomplete flow of the resin.

This working object as the anode is subjected to anodic oxidation in an aqueous oxalic acid solution (0.3 mol/L, 16°C) by application of a voltage of 40 V. In this operation, the aluminum alkoxide is gradually hydrolyzed and dissolved in the aqueous oxalic acid solution. Therefore, the electric current begins to flow firstly at the depression bottoms where the workable layer is bared, which initiates formation of the alumina nano-holes. The alumina nano-holes are formed by the anodization perpendicularly to the substrate and can readily be obtained in a high aspect ratio, which cannot be attained by usual photolithography or etching.

After immersion in an aqueous phosphoric acid solution (0.3 mol/L) for 40 minutes, regular alumina nano-holes are obtained which have a diameter of 30 nm and a depth of 500 nm.

Finally, a magnetic recording medium is obtained by filling the holes with a magnetic material by electrodeposition.

The present invention provides a process for
5 producing a nano-structure by a nano-imprinting in combination with dry-etching, wet-etching, or anodic oxidation, enabling simple production of depression type structure.